CHEMISTRY LETTERS, pp. 19-20, 1981.

STUDIES ON MOLYBDO-OXIDASE MODEL: AN EPR-EVIDENCE FOR A SIMPLE MODEL OF MOLYBDO-OXIDASE

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EPR signals due to monomeric Mo(V) species formed by mild reduction of MoO_2(cys-OR)$_2$, R = methyl, ethyl, or benzyl, were observed at 298°K and at 77°K. The EPR parameters of these complexes having catalytic activity for oxidation of triphenylphosphine are similar to those of reduced xanthine oxidase.

Active sites of molybdo-oxidases, e.g. xanthine oxidase or sulfite oxidase, have been investigated by EPR spectra resulting from the paramagnetism of mononuclear Mo(V) species[1,2]. Recently, EXAFS studies revealed presence of one or two oxo, two or three cysteine thiolates, and one nitrogen or one thioether ligands in xanthine oxidase[3]. Oxo-molybdenum(V) complexes of cysteine have attracted attention for their close connection to the active sites of these enzymes. Binuclear Mo(V) cysteine complex $[Mo_2O_4(SCH_2CH(NH_2)CO_2]^{2-}$ is well characterized and the dissociation into mononuclear Mo(V) species has been detected by the EPR spectra at pH 7-10 in water[4]. The isotopically enriched ^{95}Mo(V)-cysteine complex was reported to give the parameters: g_{av}=1.975, A_{av}=0.0054 cm^{-1}. However, the extent of this dissociation has been reported to be at best 2% and major species in water remains diamagnetic binuclear ones. Such a complex has no activity as catalyst in air oxidation. Recently, Spence et al[5] synthesized $[Et_4N][Mo^VO(C_6H_4SNCH_2CH_2NSC_6H_4)]$, which gives the following EPR parameters: g_x=1.974, g_y=1.977, g_z=2.005, A_z=0.00569 cm^{-1} (for ^{95,97}Mo).

$MoO_2(S_2CNEt_2)_2$ has been found to oxidize tertiary phosphines to give phosphine oxides and $Mo_2O_3(S_2CNEt_2)_4$[6-10]. Newton[11] proposed a mechanism involving O-atom transfer to give $Mo^{IV}O(S_2CNEt_2)_2$ which rapidly combines with $MoO_2(S_2CNEt_2)_2$. No mononuclear EPR active species is involved. Speier[12] also has speculated the same mechanism for the oxidation of various alkylphosphines by MoO_2(cys-OEt)$_2$.

We have obtained evidence for the mononuclear Mo(V) cysteinate alkyl ester complex as a stable abundant solution species, which shows EPR spectra similar to the ones observed for molybdo-oxidase. Figure 1 shows the EPR signals for the reduction species of MoO_2(cys-OEt)$_2$ formed by addition of excess PPh_3 in dimethylformamide(DMF)/water(10:1). The g values, g_{av}=1.972, A=0.0033 cm^{-1}(for $^{95,97}Mo$) at 25° observed in our case are similar to the g_{av}=1.977, A=0.0034 cm^{-1}(for ^{95}Mo) for xanthine oxidase[1]. The result was interpreted to indicate the S,N chelation to the Mo(V) atom. The hyperfine splitting due to $^{95,97}Mo$ indicates that the species is mononuclear in solution similar to the Mo-site of the enzyme.

The formation of such a paramagnetic Mo(V) species is supported by the ^{13}C NMR spectra in dimethyl sulfoxide-d_6. The carbon peak due to the cysteine CH_2S group disappeared in 5 h and strong EPR signals shown in Fig. 1 appeared. Similar spectroscopic behavior was also observed with MoO_2(cys-OMe)$_2$ or MoO_2(cys-OBzl)$_2$. However, no EPR signal was observed upon reduction of $MoO_2(S_2CNEt_2)_2$ by excess PPh_3 in DMF/water. $Mo^{V}_{2}O_{3}$($S_2CNEt_2)_4$ and/or $Mo^{IV}O(S_2CNEt_2)_2$ are formed in this case.

Thiolate-chelated monomeric Mo(V) species are active in the catalytic air oxidation of PPh_3 in DMF/water[13] and thus important as a model of molybdo-oxidases.

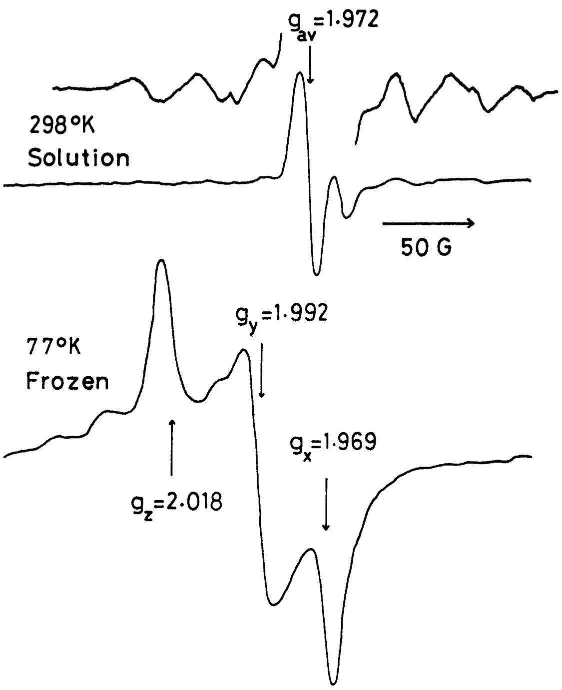

Figure 1 EPR spectra of reduced MoO_2(cys-OEt)$_2$ in DMF/water.

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(Received October 6, 1980)